Excess Enthalpies for 1,1,1-Trichloroethane with Alkanes, Ketones, and Esters

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Excess enthalpies provide quantitative information about the temperature dependence of the excess Gibbs energy G^E. This information should therefore be used together with other results (vapor–liquid equilibria, liquid–liquid equilibria, limiting activity coefficients, and azeotropic data) for fitting simultaneously temperature-dependent G^E model parameters or interaction parameters of group contribution methods. Although a large number of H^E measurements have been published, results at temperatures other than 298.15 K are scarce. In this paper a flow calorimeter is described, and excess enthalpy data are given for the test systems *n*-hexane + cyclohexane, benzene + cyclohexane, and methanol + water at 298.15 K as well as for 1,1,1-trichloroethane + *n*-pentane, + *n*-heptane, + acetone, + 2-butanone, + methyl acetate, and + ethyl acetate at 363.15 K. The results were used for the systematic development of the group contribution method (modified UNIFAC) developed at Dortmund.

Introduction

The Gibbs–Helmholtz relation together with information on excess enthalpies allows a quantitative temperature extrapolation of the excess Gibbs energy G^E or activity coefficients. Excess enthalpies (H^E) should therefore be used for fitting reliable G^E model parameters or the required group interaction parameters for group contribution methods.

Approximately 8400 H^E data sets are available in the literature (*4, 5*). The distribution of these sets as a function of temperature is shown in Figure 1; it can be seen that the majority of H^E measurements have been made within the temperature range 283–323 K.

While in the case of the original UNIFAC method (*1*) vapor–liquid equilibrium (VLE) data (and sometimes liquid–liquid equilibrium (LLE)) were primarily used to fit the temperature-independent group interaction parameters, in the modified UNIFAC (Dortmund) version (*2, 3*) not only VLE results but also excess enthalpies and limiting activity coefficients have been used to fit the temperature-dependent parameters.

Excess enthalpies over a wide temperature range would be desirable for refining the group interaction parameters. Furthermore, measurements for a large number of group combinations are not available. An isothermal flow calorimeter has previously been used to measure excess enthalpy data for many of these mixtures at temperatures outside the range 283–323 K in order to permit the systematic development of the modified UNIFAC (Dortmund) method (*3*). In this paper the results for three test systems (*n*-hexane + cyclohexane, benzene + cyclohexane, methanol + water) and for 1,1,1-trichloroethane + *n*-pentane, + *n*-heptane, + acetone, + 2-butanone, + methyl acetate, and + ethyl acetate at 363.15 K are reported. The test systems were chosen to check the reliability of the flow calorimeter. The results for mixtures with 1,1,1-trichloroethane have been used to fit the group interaction parameters for the new main group CCl3 (different from the main group CHCl3) used in the modified UNIFAC (Dortmund) method (*3*).

Experimental Procedure

A commercially available flow calorimeter from Hart Scientific (model 7501) was used for the measurements of the excess enthalpies. The calorimeter consists of two solvent pumps (ISCO, LC 2600, 260 cm^3), a thermostated flow cell, and a back pressure regulator to prevent evaporation.

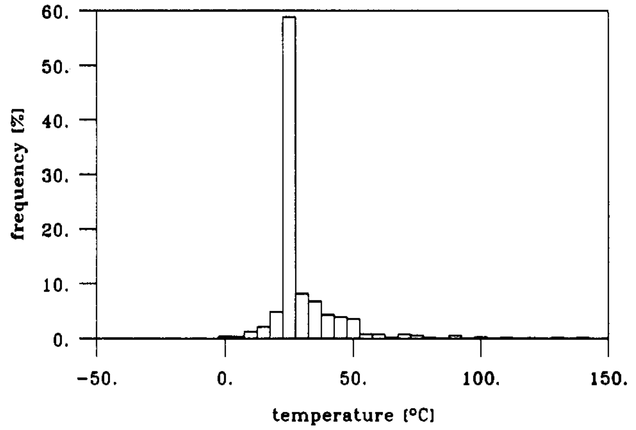

Figure 1. Temperature distribution of experimental excess enthalpies stored in the Dortmund Data Bank (DDB).

The flow cell with a pulsed heater, a calibration heater, a Peltier cooler, and a mixing tube wound around a copper cylinder (*6*) is located in a stainless steel cylinder which is immersed in a thermostat. The combination Peltier cooler/pulsed heater allows not only the determination of endothermic effects but also exothermic effects. Depending on the H^E values and the flow rate for the different systems, the power per pulse can be varied between 0.05 and 20 μJ. The energy per pulse can be obtained by calibration using the energy dissipated from a precise resistor fixed at the cylinder of the flow cell. Silicon oil is used as the thermostating liquid, so that the equipment can be used over the temperature range 273–453 K; the pressure can be kept constant at up to 140 bars. The calorimeter assembly is shown in Figure 2.

A constant temperature of the flow cell is realized by adjusting the frequency of the pulsed heater to balance the cooling from the Peltier cooler. The pressure is kept constant by a back pressure regulator. The temperatures of the liquid pumps and the thermostat are monitored with a Hart Scientific platinum resistance thermometer (model 1006 Micro-Therm) with an accuracy of ±0.005 K. The calibrated liquid pumps were maintained at 298.15 K for all systems studied.

After a stable base line (constant frequency of the pulsed heater) was obtained for various flow rates the measurements

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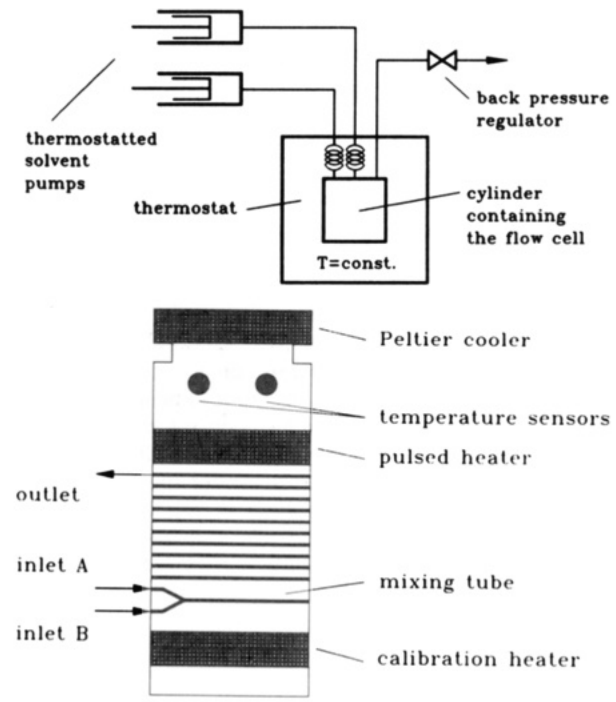

Figure 2. Diagram of the flow calorimeter.

Table I. Excess Enthalpies for Test Systems at 298.15 K

x_1	$H^E/(\mathrm{J\ mol^{-1}})$	x_1	$H^E/(\mathrm{J\ mol^{-1}})$	x_1	$H^E/(\mathrm{J\ mol^{-1}})$
n-Hexane (1) + Cyclohexane (2)					
0.0525	59.1	0.3328	213.2	0.6465	181.0
0.1061	108.3	0.3927	220.3	0.7138	158.4
0.1609	147.8	0.4539	220.2	0.7827	126.9
0.2170	177.2	0.5166	212.8	0.8533	90.2
0.2742	198.3	0.5808	199.9	0.9258	47.9
Benzene (1) + Cyclohexane (2)					
0.1197	330.6	0.4492	795.7	0.7406	636.9
0.2342	569.6	0.5503	805.2	0.8303	477.9
0.3440	717.8	0.6473	749.3	0.9167	263.5
Methanol (1) + Water (2)					
0.0253	−172.5	0.3554	−883.9	0.5696	−752.1
0.0523	−335.0	0.3554	−884.1	0.6069	−717.7
0.0811	−484.4	0.4094	−862.9	0.6880	−617.6
0.1450	−713.4	0.5342	−782.2	0.7792	−489.0
0.2192	−842.8	0.5696	−749.4	0.8823	−287.0
0.2608	−876.3	0.5696	−744.5	0.9392	−138.5
0.3061	−888.9				

were made under computer control. During the measurements for a chosen total flow rate, the frequency of the pulsed heater was recorded for approximately 2000 s. This procedure was continued for different flow rates of the individual compounds until the liquid pumps were emptied. After the pumps were refilled a second series of measurements were made. Flow rates were selected to cover the whole mole fraction range. In most cases the experiments were made with a total flow rate of 80 cm^3 h^{-1}.

From the recorded frequency change of the pulsed heater and the flow rates, the molar excess enthalpies were obtained from the energy evolved per pulse, the pure component densities at 298.15 K, and the molar mass of the compounds. The uncertainty in H^E was estimated to be less than ±1%.

Experimental Results

The results for the test systems at 298.15 K and the mixtures with 1,1,1-trichloroethane at 363.15 K are given in Tables I and II. The results have been fitted to the Redlich–Kister equation

Table II. Excess Enthalpies for Mixtures Containing 1,1,1-Trichloroethane at 363.15 K

x_1	$H^E/(\mathrm{J\ mol^{-1}})$	x_1	$H^E/(\mathrm{J\ mol^{-1}})$	x_1	$H^E/(\mathrm{J\ mol^{-1}})$
n-Pentane (1) + 1,1,1-Trichloroethane (2)					
0.0548	85.2	0.3129	353.7	0.7229	332.5
0.1105	162.0	0.4035	396.6	0.7229	330.3
0.1105	162.0	0.4651	410.6	0.7767	287.2
0.1786	241.8	0.4651	408.1	0.7767	287.7
0.1786	241.3	0.4651	408.4	0.8589	201.3
0.2247	287.5	0.5279	412.6	0.8589	202.7
0.2247	287.1	0.6241	388.0	0.9288	110.8
1,1,1-Trichloroethane (1) + *n*-Heptane (2)					
0.0887	145.5	0.4670	485.0	0.7360	405.6
0.1726	262.4	0.5318	494.7	0.8142	321.7
0.1726	264.6	0.5936	485.7	0.8539	267.5
0.2675	367.3	0.5936	482.9	0.9109	177.0
0.2675	367.9	0.6525	462.6	0.9109	176.9
0.3274	418.2	0.7088	424.4	0.9563	91.1
Acetone (1) + 1,1,1-Trichloroethane (2)					
0.0833	73.3	0.4500	227.0	0.8451	118.4
0.1630	132.0	0.5769	221.3	0.9052	77.9
0.1630	132.2	0.5769	221.1	0.9052	77.6
0.2542	179.7	0.6944	191.7	0.9534	40.1
0.3125	202.1	0.8036	143.5		
1,1,1-Trichloroethane (1) + 2-Butanone (2)					
0.1144	−11.73	0.4747	−27.18	0.7966	−12.64
0.1726	−16.81	0.6010	−24.57	0.8635	−8.26
0.2315	−21.08	0.7306	−17.05	0.9313	−3.60
0.3516	−26.37	0.7966	−12.66		
Methyl Acetate (1) + 1,1,1-Trichloroethane (2)					
0.0778	42.11	0.4314	163.56	0.7914	124.72
0.1530	78.95	0.4959	171.06	0.8349	105.47
0.1530	78.61	0.5584	171.31	0.8349	105.85
0.2402	114.11	0.5584	170.96	0.8985	70.71
0.2965	132.94	0.6192	168.38	0.8985	71.17
0.3985	159.22	0.6782	157.53	0.9499	37.67
1,1,1-Trichloroethane (1) + Ethyl Acetate (2)					
0.0611	−18.14	0.3692	−88.49	0.7453	−85.68
0.1223	−35.17	0.4314	−96.50	0.7960	−74.44
0.1223	−35.64	0.4938	−100.79	0.8723	−52.67
0.1961	−54.75	0.5564	−102.68	0.8723	−53.31
0.1961	−54.47	0.6192	−100.83	0.9360	−29.34
0.2454	−66.36	0.6506	−98.30		

$$H^E/(x_1x_2) = \sum_{i=1}^{m} A_i(2x_1 - 1)^{i-1}$$

and the following objective function (*4*):

$$F = \sum[(H^E/x_1x_2)_{\mathrm{exptl}} - (H^E/x_1x_2)_{\mathrm{calcd}}]^2$$

$$j = 1, 2, ..., n$$

The Redlich–Kister parameters are given in Table III. In Figures 3–5 the H^E results for the test systems *n*-hexane + cyclohexane, benzene + cyclohexane, and methanol + water at 25 °C are compared with the results of other researchers (*7–9*). From all three diagrams it can be seen that our results within ± 1% agree with those obtained by other research groups.

The excess enthalpy results for mixtures containing 1,1,1-trichloroethane were used to check if a new main group (CCl3) should be defined or if compounds similar to 1,1,1-trichloroethane can be combined with results for chloroform systems (as done in most group contribution methods) to fit the required group interaction parameters.

Binary ketone + chloroform and ester + chloroform systems in particular are well known to show negative deviations from Raoult's law and to have large negative excess enthalpies. Apart from the systems with hydrocarbons (*n*-pentane,

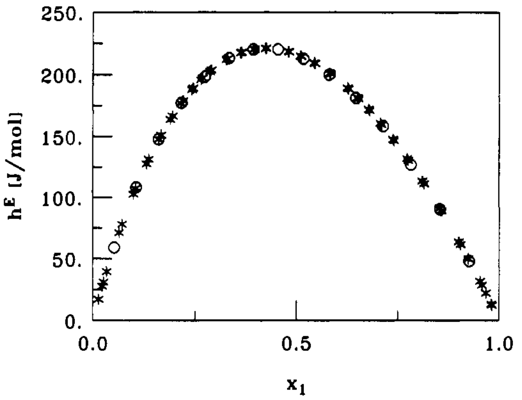

Figure 3. H^E data for *n*-hexane (1) + cyclohexane (2) at 298.15 K: (*) data from ref 7, (O) present results.

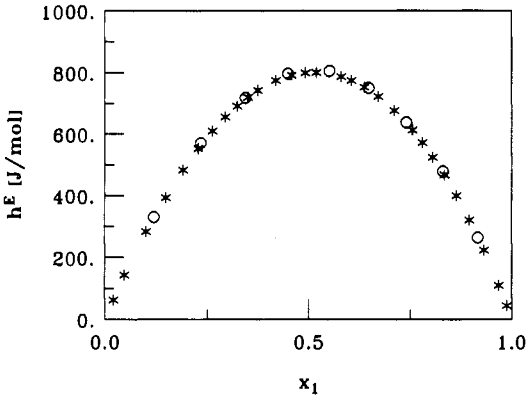

Figure 4. H^E data for benzene (1) + cyclohexane (2) at 298.15 K: (*) data from ref 8, (O) present results.

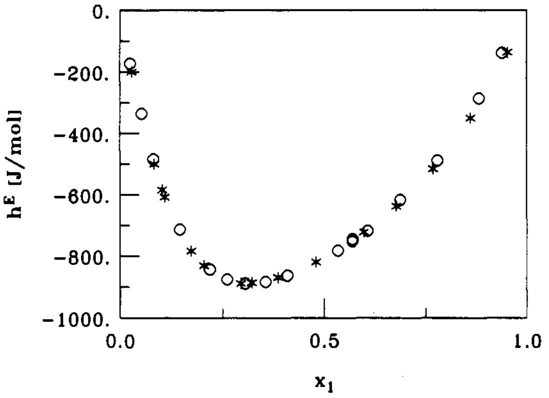

Figure 5. H^E data for methanol (1) + water (2) at 298.15 K: (*) data from ref 9, (O) present results.

n-heptane) the H^E values for trichloroethane with ketones (acetone, 2-butanone) and esters (methyl acetate, ethyl acetate) were also investigated. Figures 6 and 7 show the results for the ketone systems together with the predicted results of the different group contribution methods (*10–12*).

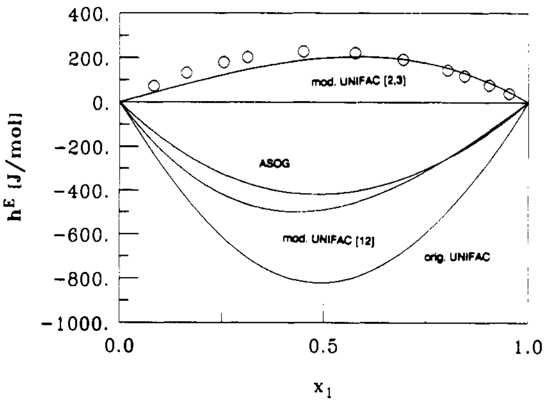

Figure 6. Experimental and predicted H^E values for acetone (1) + 1,1,1-trichloroethane (2) at 363.15 K.

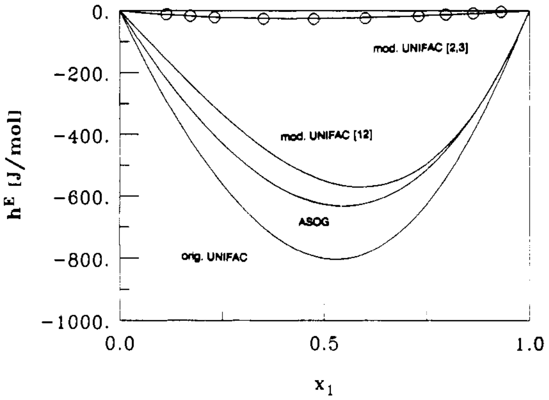

Figure 7. Experimental and predicted H^E values for 1,1,1-trichloroethane (1) + 2-butanone (2) at 363.15 K.

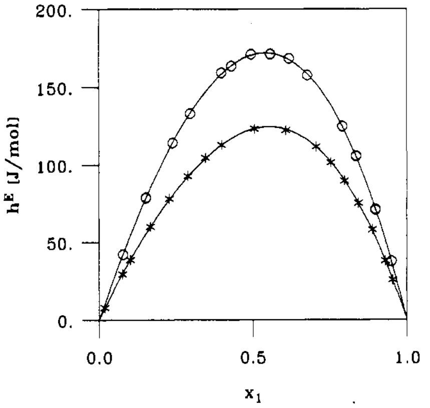

Figure 8. Experimental H^E results for methyl acetate (1) + 1,1,1-trichloroethane (2): (*) data from ref 13 at 298.15 K, (O) present results at 363.15 K.

Only the modified UNIFAC (Dortmund) method, which contains a special group for chloroform, is able to describe the experimental H^E results. Hence, it is important to include a main group CCl_3, as well as the special group chloroform

Table III. Redlich–Kister Parameters

component 1	component 2	T/K	A_1	A_2	A_3	A_4	A_5	A_6	RMSD/ (J mol^{-1})
n-hexane	cyclohexane	298.15	861.15	-253.81	113.42	-32.13	-19.157		0.53
benzene	cyclohexane	298.15	3229.9	141.93	86.753	75.241			1.45
methanol	water	298.15	-3196.1	1395.2	-2645.7	1639.5	1131.3	-459.65	5.42
n-pentane	1,1,1-trichloroethane	363.15	1647.6	6.3386	18.044	13.703			0.83
1,1,1-trichloroethane	*n*-heptane	363.15	1963.7	-215.26	98.482	-16.471	-95.594		1.08
acetone	1,1,1-trichloroethane	363.15	917.14	-51.953	30.377	18.242			0.78
1,1,1-trichloroethane	2-butanone	363.15	-108.89	33.181	30.857				0.18
methyl acetate	1,1,1-trichloroethane	363.15	682.78	113.20	20.075	5.3475	-21.652		0.46
1,1,1-trichloroethane	ethyl acetate	363.15	-405.28	90.563	3.0436	11.273			0.21

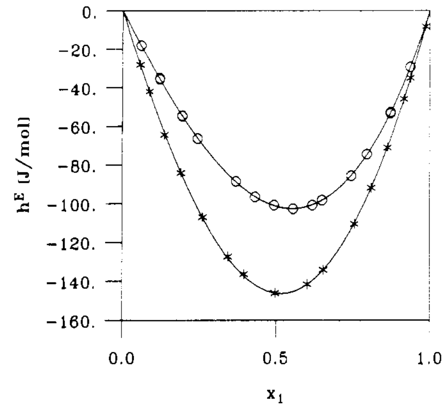

Figure 9. Experimental H^E results for 1,1,1-trichloroethane (1) + ethyl acetate (2): (*) data from ref 13 at 298.15 K, (O) present results at 363.15 K.

in the modified UNIFAC method, although the addition of a new main group means that the parameters with all other main groups have to be fitted.

Since no VLE measurements have been made on 1,1,1-trichloroethane + esters, no group interaction parameters could be fitted. The results for the ester systems are shown in Figure 8 and 9 together with those published by other researchers (*13*).

Conclusion

Excess enthalpies were measured for mixtures containing 1,1,1-trichloroethane at 363.15 K with the objective of extending the excess enthalpy data base for the further development of the modified UNIFAC method. Up to now more than 120 isothermal H^E data sets have been measured using the technique described.

This paper contains the results for different test systems as well as H^E data for binary systems containing 1,1,1-trichloroethane and alkanes (*n*-pentane, *n*-heptane), ketones (acetone, 2-butanone), or esters (methyl acetate, ethyl acetate) at 363.15 K. The measurements reported were used to fit the group interaction parameters for the new main group "CCl3" in the modified UNIFAC (Dortmund) method. The other excess enthalpy measurements will be published in ref 14.

Acknowledgment

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Glossary

A_i	parameters used in the Redlich-Kister expansion
G^E	molar excess Gibbs energy
H^E	molar heat of mixing
m	number of fitted Redlich-Kister parameters
n	number of experimental data points
x_i	mole fraction of component i in the liquid phase
γ	activity coefficient

Superscripts

∞	value at infinite dilution
E	excess property

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